

Current Distribution and Mass Transfer in Electrochemical Systems

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Fundamental equations describing transport in dilute electrolytic solutions have been known since the turn of the century. In an electrochemical system, many processes occur simultaneously, and the treatment of such systems involves consideration of the ohmic potential drop, concentration changes near electrodes, and the kinetics of the heterogeneous electrode reaction.

Application of these principles has followed two main courses. There are systems where the ohmic potential drop can be neglected. The current distribution is then determined by the same principles which apply to heat transfer and non-electrolytic mass transfer. This usually involves systems operated at the limiting current with an excess of supporting electrolyte. Let us call these "convective-transport problems."

At currents much below the limiting current it is possible to neglect concentration variations near the electrodes. The current distribution is then determined by the ohmic potential drop in the solution and by electrode overpotentials. Mathematically, this means that the potential satisfies Laplace's equation, and many results of potential theory, developed in electrostatics, the flow of inviscid fluids, and steady heat conduction in solids, are directly applicable. Let us call these "potential-theory problems." The electrode kinetics provide boundary conditions which are usually different from those encountered in other applications of potential theory.

Problems have been treated which do not fall within either of these two classes. First, there are "intermediate problems," where convective transport is essential but neither concentration variations near the electrode nor the ohmic potential drop in the solution can be neglected. These involve currents below, but at an appreciable fraction of, the limiting current.

Some problems are not so general, but can be regarded as an extension of the convective-transport problems. At the limiting current the ohmic potential drop in the bulk of the solution may still be negligible, but the electric field in the diffusion layer near electrodes may lead to an enhancement of the limiting current. The current may then be distributed in a similar fashion, but the magnitude is changed.

In porous electrodes convection may not be present, but it is usually necessary to consider the ohmic potential drop, concentration variations, and electrode kinetics. Most treatments adopt a macroscopic model which does not take account of the detailed, random geometry of the porous structure. Results of potential theory are then not applicable since Laplace's equation does not hold.

Transport in electrolytic solutions. The concentration and potential distributions are to be determined from the equations

$$\underline{N}_i = -z_i u_i F c_i \nabla \Phi - D_i \nabla c_i + y c_i \quad (1)$$

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \underline{N}_i, \quad \underline{i} = F \sum_i z_i \underline{N}_i, \quad \sum_i z_i c_i = 0 \quad (2,3,4)$$

The first states that species in the solution can move by migration, diffusion, and convection. The second is a material balance for a species. The third states

that the current arises from the motion of charged particles. The fourth is the condition of electroneutrality. These laws provide the basis for the analysis of electrochemical systems. The fluid velocity is to be determined from the laws of fluid mechanics.

Electrode kinetics. The differential equations describing the electrolytic solution require boundary conditions in order for the behavior of an electrochemical system to be predicted. The most complex of these concerns the kinetics of electrode reactions and relates the normal component of the current density at an electrode to the surface overpotential. The surface overpotential η_s can be defined as the potential of the working electrode relative to a reference electrode of the same kind located just outside the double layer.

There is no completely general expression describing electrode kinetics. However, it is adequate for our present purpose to assume that the current density depends exponentially on the surface overpotential in the following form:

$$i = i_0 \left[\exp \left\{ \frac{\alpha n F}{RT} \eta_s \right\} - \exp \left\{ - \frac{(1-\alpha) n F}{RT} \eta_s \right\} \right]. \quad (5)$$

Convective-transport problems. For the reaction of minor ionic species in a solution containing excess supporting electrolyte, it should be permissible to neglect the contribution of ionic migration to the flux of the reacting ions, so that equation (1) becomes

$$\underline{N}_i = -D_i \nabla c_i + \underline{v} c_i, \quad (6)$$

and substitution into equation (2) yields

$$\frac{\partial c_i}{\partial t} + \underline{v} \cdot \nabla c_i = D_i \nabla^2 c_i. \quad (7)$$

This may be called the equation of convective diffusion. A similar equation applies to convective heat transfer and convective mass transfer in non-electrolytic solutions. Since these fields have been studied in detail, it is possible to apply many results to electrochemical systems which obey equation (7).

The systems typically studied in heat and mass transfer involve laminar and turbulent flow with various geometric arrangements. The flow may be due to some more or less well characterized stirring (forced convection) or may be the result of density differences created in the solution as part of the transfer process (free convection).

Essential to the understanding of convective-transport problems is the concept of the diffusion layer. Frequently, due to the small value of the diffusion coefficient, the concentrations differ significantly from their bulk values only in a thin region near the surface of an electrode. In this region the velocity is small, and diffusion is important to the transport process. The thinness of this region permits a simplification in the analysis, but it is erroneous to treat the diffusion layer as a stagnant region. Figure 1 shows the concentration profile in the diffusion layer, with the electrode surface at the left. Far from the surface convective transport dominates, while at the surface itself there is only diffusion.

To illustrate the current distribution obtained in this type of problem, consider two plane electrodes of length L and separated by a distance h and which form parts of the walls of a flow channel with otherwise insulating walls. For laminar flow from left to right, with an average velocity $\langle v \rangle$, the limiting current density has the distribution, as illustrated in figure 2,

$$i = 0.9783 \frac{nF D_i c_\infty}{s_i} \left(\frac{\langle \nabla \rangle}{h D_i x} \right)^{1/3}, \quad (8)$$

where x is the distance along the electrode. The mass-transfer rate is infinite at the upstream edge of the electrode where fresh solution is brought in contact with the electrode. The current decreases with increasing x since the solution in the diffusion layer has already been depleted by the electrode reaction further upstream. Later it will be instructive to compare this current distribution with that which would be obtained when the ohmic potential drop in the solution is controlling.

Other convective-transport problems which have been treated include flow in a pipe and in annular conduits, a flat plate in a free stream, rotating cylinders, growing mercury drops, rotating disks, and free convection at vertical and horizontal plates and outside spheres and cylinders.

Applications of potential theory. When concentration gradients in the solution can be ignored, equations (3), (1), and (4) yield

$$\underline{i} = -\kappa \nabla \Phi \quad (9)$$

where

$$\kappa = F^2 \sum_i z_i^2 u_i c_i \quad (10)$$

is the conductivity of the solution. Equation (2) when multiplied by z_i and summed over i yields

$$\nabla^2 \Phi = 0, \quad (11)$$

that is, the potential satisfies Laplace's equation.

The boundary conditions are determined with equation (9). On insulators

$$\partial \Phi / \partial y = 0, \quad (12)$$

where y is the normal distance from the surface. On electrodes, equation (9) relates this potential derivative to the surface overpotential through equation (5). If the potential Φ in the solution is measured with a reference electrode of the same kind as the working electrode, then the surface overpotential can be eliminated with the relation

$$\eta_s = V - \Phi, \quad (13)$$

where V is the potential of the metal electrode. The resulting boundary condition is a nonlinear relationship between the potential and the potential derivative and is not commonly encountered in other applications of potential theory.

In so-called primary-current-distribution problems the surface overpotential is neglected altogether, and the solution adjacent to the electrode is taken to be an equipotential surface. The resulting current distribution for the plane electrodes in the flow channel considered earlier is shown in figure 2 for $L = 2h$. The distribution is symmetric since convection is not important. The current density is infinite at the ends of the electrodes since the current can flow through the solution beyond the ends of the electrodes. This is a general characteristic of primary current distributions. The current density where an electrode meets an insulator is either infinite or zero unless they form a right angle.

The so-called secondary current distribution takes into account the surface overpotential, although the boundary condition is frequently replaced by a linear or a logarithmic (Tafel) relation between the potential and the potential derivative. The general effect of electrode polarization is to make the secondary current distribution more nearly uniform than the primary current distribution, and an infinite current density at the edge of electrodes is eliminated.

Intermediate problems. The current distribution on a rotating disk electrode¹ and free convection on two vertical electrodes at either end of a rectangular tank² have been treated with account taken of concentration variations, ohmic potential drop, and surface overpotential. The results are, as one might expect, intermediate between the two extreme cases. The formulation of the problem so as to take advantage of the thinness of the diffusion layer has also been discussed.³

Effect of migration on limiting currents. At the limiting current, the current density is distributed along the electrode in the same manner as when migration is neglected, but the magnitude of the current density at all points is increased or diminished by a constant factor which depends upon the bulk composition of the solution. This effect has been treated^{3,4} for the rotating disk, the growing mercury drop, penetration into a semi-infinite medium, the stagnant Nernst diffusion layer, and arbitrary two-dimensional and axisymmetric diffusion layers.

¹ John Newman. "Current Distribution on a Rotating Disk below the Limiting Current." Journal of the Electrochemical Society, 113, 1235-1241 (1966).

² Kameo Asada, Fumio Hine, Shiro Yoshizawa, and Shinzo Okada. "Mass Transfer and Current Distribution under Free Convection Conditions." Journal of the Electrochemical Society, 107, 242-246 (1960).

³ John Newman. The Effect of Migration in Laminar Boundary Layers. UCRL-16665-Rev. December, 1966.

⁴ John Newman. "Effect of Ionic Migration on Limiting Currents." Industrial and Engineering Chemistry Fundamentals, 5, 525-529 (1966).

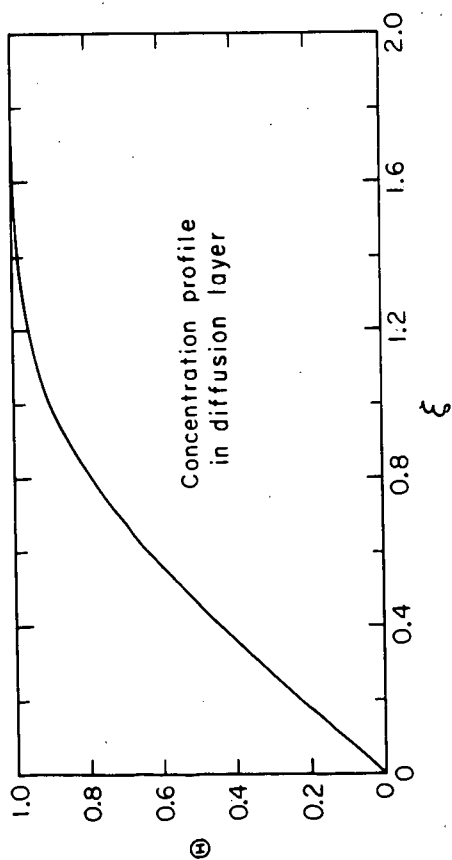


Figure 1.

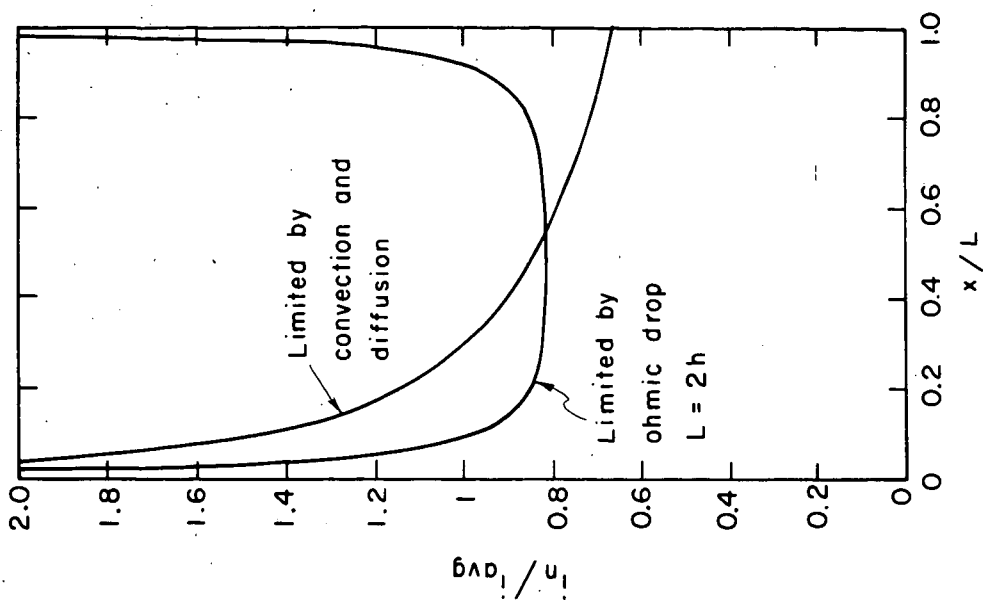


Figure 1. Current distribution on planar electrodes.